Indian J. Phys. **68A** (3), 297 – 300 (1994)

I J P A
— an international journal

EPR of γ-irradiated imidazole complex $Cd(Im)_3SO_4.H_2O$

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Received 8 September 1993, accepted 31 January 1994

Abstract : The EPR spectra of γ-irradiated single crystals of the imidazole ligated $Cd(Im)_3SO_4 H_2O$ are studied at 300 K. From the analysis of EPR spectra the major radical formed is identified to be hydroimidazole originating from the damaged ligand. No cadmium based radical is detected.

Keywords : Cd-imidazole complex, γ-irradiation, hydroimidazole, EPR

PACS No. : 76.30.Rn

Study of imidazole complexes is of interest due to the biological significance of the binding of metal ions with the imidazole ring of the histidine unit which occurs in a large number of proteins and enzymes [1,2]. EPR has given information on the site symmetry and metal-ligand bonding in a number of paramagnetic metal ions doped single crystals of diamagnetic imidazole host complexes [3–6]. Pure imidazole crystal [7] and alkyl derivatives of imidazole [8] have also been subjected to ionising radiations and the structure of the products studied by EPR technique. The present study tries to explore the structure of radicals produced by γ-irradiation of single crystals of $Cd(Im)_3SO_4.H_2O$ by EPR spectroscopy. The main radical produced is identified to be a hydroimidazole radical.

The complex $Cd(Im)_3SO_4.H_2O$ was obtained by mixing 1 M aqueous solutions of cadmium sulphate and imidazole in the ratio of 1 : 2 at a pH of 7.5 adjusted with 6 M H_2SO_4. Slow evaporation of this solution gives well-defined single crystals within a week. Single crystals were irradiated in a gamma cell with an effective dose rate of 0.35 M rad h^{-1} for a

period of 4–6 hours at 300 K. EPR measurements were carried out at 300 K on a Varian E-4 X-band spectrometer.

The crystal structure of $Cd(Im)_3SO_4.H_2O$ has been determined by Cairo *et al* [9]. The crystal symmetry is monoclinic and the space group is $P2_1/n$. The Cd atom is bonded to three nitrogen atoms from three imidazole rings, a hydrated oxygen and the oxygen from a sulphate group (Figure 1a). There are two polymer chains in the cell, one of which is illustrated in Figure 1b. Each chain is arranged in a helix about the 2_1 axis and hydrogen bonding exists within the polymer chains and also in between the chains.

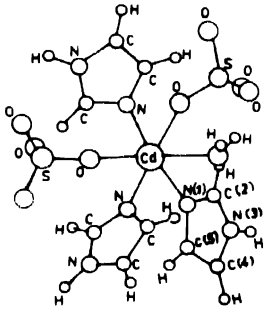

Figure 1(a). Coordination around Cd(II) in $Cd(Im)_3SO_4\,H_2O$

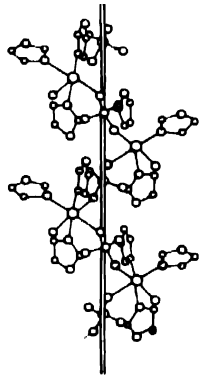

Figure 1(b). One of the polymer chains about the screw axis

EPR spectra of single crystals of $Cd(Im)_3SO_4.H_2O$ γ-irradiated at 300 K were taken in the three reference planes a^*b, bc and ac. Spectra were obtained at 10° intervals in each plane by successive rotations of the crystal. The centre of gravity of the spectrum gives the g value varying from 2.0024 to 2.0036, indicating the organic nature of the radical. The different orientations of the three imidazole rings in a single molecular site, make the spectra more complex even for the rotation about the b-axis where a single magnetic site is expected However in all orientations, a major triplet with an intensity of 1 : 2 : 1 is seen (Figure 2). The triplet can arise only from a free radical containing two magnetically equivalent nuclei of spin $I = 1/2$ and in the present case, protons. The triplet spacing, followed in three different planes, is found to vary in a small range of 45–50 G. This value compares very well with those obtained for the radical originating from pure imidazole crystals on γ-irradiation [7,10]. In organic radicals, α-proton hyperfine coupling (inclusive of both dipolar and isotropic part) is expected to be of 33 G for unit spin density on the p-orbital of carbon [11]. However, if the proton hyperfine splitting arises *via* hyperconjugation as found in β-protons, then the hyperfine coupling constant can be higher as in the case of cyclohexadienyl radical [12] Further if the hyperfine interaction arises due to hyperconjugation, then the dipolar coupling is expected to be very small and negligible [13]. On the basis of these arguments, the major *hf*

triplet seen in Figure 2 may be attributed to a dienyl type radical which could be produced as a result of partial hydrogenation of a double bond in the ligand imidazole molecule. The radical thus formed, can have CH_2 fragments capable of hyperconjugative hyperfine interactions with the unpaired electron cloud.

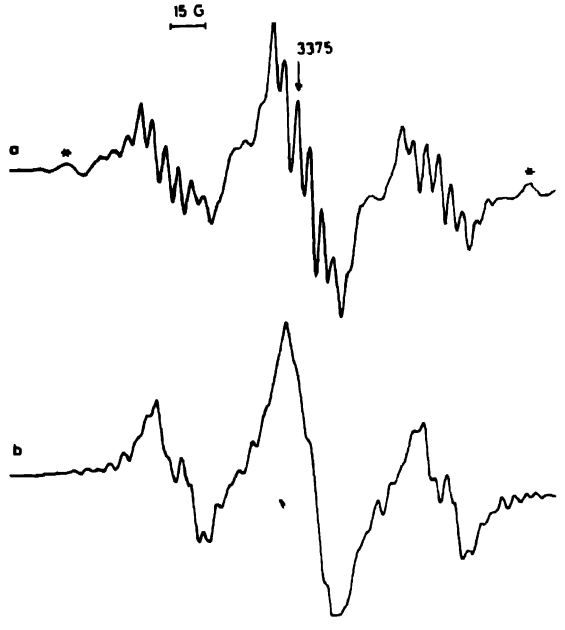

Figure 2 (a) and (b). EPR spectra at 300 K of the hydroimidazole radical for two orientations when the rotation is about *b*-axis. (* Features unidentified)

The point of hydrogenation can be either C_2, C_4 or C_5, all of which can lead to radical containing a CH_2 fragment adjacent to a delocalised system.γ-irradiation of imidazole crystal at 300 K gives a similar radical [7,10]. Analysing the spectra obtained from the radiation damage of the undeuterated and the various deuterated imidazoles, Lamotte and Gloux [7] have established that the hydrogen addition must occur on the carbon C_2. Hence, we propose that the hydroimidazole radical formed in the present case is also the same with hydrogen addition on C_2.

In addition to the major triplet, other signals such as the one marked with * mark in Figure 2a were also observed. However, these lines were burried under the major triplet in most of the orientations. The number of possible sites due to the very reduced symmetry of the crystal leads to overlap of many lines, thus preventing a complete analysis of the spectrum.

From the EPR spectra, it may be concluded that the radiation damage of the complex $Cd(Im)_3SO_4.H_2O$, results in a carbon–hydrogen bond cleavage in the imidazole moiety. Partial hydrogenation at carbon C_2 produces a hydroimidazole radical. The delocalized unpaired electron in the orbital, leads to hyperconjugative interaction with the CH_2 protons.

Acknowledgment

Thanks are due to Regional Sophisticated Instrumentation Centre, IIT, Madras for instrumental facilities and to Prof S Subramanian for discussions.

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